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SINTERING PARTICULARS FOR CERAMIC MATERIALS

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The integral and local compaction occurring during sintering of ceramic materials are analyzed. A model describing the structure of the material during the sintering process taking account of clusterization of the components of the particle material is proposed. Relations and an algorithm for calculating the micro- and macroporosity space (coordination number, specific surface, and average pore size) are obtained. Calculations performed with this model showed that the macropore size increases sharply at the beginning of the sintering process.

Key words: model, structure, interparticle contact, micro- and macroporosity, particle size, specific surface, pore radius, coordination number, sintering.

Sintering of ceramic and porous ceramic materials determines their structure and properties, i.e., article quality.

The material is not uniform during sintering because of clusterization, i.e., local compaction, in certain zones. The interconnection of these zones breaks down partially or completely. As a result the macroscopic volumetric changes lag behind the changes in the local parts of the system [1-6]. Clusterization is characteristic mainly for the initial stage of sintering, and its intensity is determined by the degree of nonuniformity of the initial porous structure [5, 6] and the kinetic process [3-5]. It manifests as an increase in the average pore size, which decreases the shrinkage of the material [5]. In addition, the work in [7] should be taken into account indirectly. According to [7] the change in the structure of the solid phase of a material and the porous structure mainly proceeds in different directions (as the porosity decreases the coordination number Z increases in the solid phase of a material and decreases in the porous structure). In the process a biporous structure forms during the sintering process [4, 8, 9].

The sintering process for powders has been analyzed in [5], where the magnitudes of the local and macroscopic compactions were determined from the shrinkage of a porous body as a whole and the average pore size. In [5] it was assumed that at the first (hypothetical) stage the initial number of pores is conserved and the shrinkage $\Delta V/V_m$ (where ΔV is the volume change and V_m the initial volume of the material) is due to a decrease in the pore size. At this stage uniform

compaction (sintering) promotes a uniform reduction of the diameter of all pores.

At the second stage the total pore volume is conserved (there is no additional macroscopic shrinkage), and the average pore radius r increases from the initial value r_m to the experimentally determined value with the corresponding decrease in the number of pores. This stage is due to additional redistribution of the material with a reduction of the free surface but no macroscopic shrinkage.

However, in the method the structural model of the material in the form of uniformly distributed isolated spherical pores of the same size is idealized. Such a model does not reflect the real structure of a porous material and the character of the change in the structure, which is an impediment to its use

A more accurate model in the form of a three-dimensional capillary network with average radius *r* taking account of the cluster porosity is more expedient.

For this three-dimensional model it is possible to calculate the pre-sintering shrinkage of the material from the initial porosity of the molded green body Π_m to the post-sintering porosity Π and to determine the average post-sintering size r of the pores (capillaries) according to the known initial value r_m .

A unit volume of the initial system consists of a solid phase V_s and pores $V_{mp} = \pi n L_m r_m^2$, where L_m and n are, respectively, the average length and number of individual pores (capillaries) in this volume before sintering.

The porosity decreases during the sintering process. The relative shrinkage of the material $\Delta V/V_m$ is given by $\Delta V/V_m = (\Pi - \Pi_m)/(1 - \Pi)$. We note that the pore sizes and

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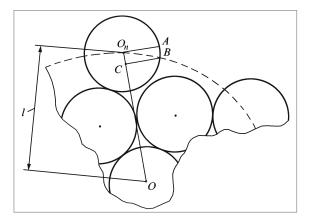


Fig. 1. Fragment of the cross section of a cluster.

the shrinkage of the material are interrelated nonlinearly owing to the clusterization process.

We shall examine the calculation of the change in the structural parameters of powder material during sintering for a monodisperse material comprised of particles with diameter D. The average structural parameters (porosity Π , average coordination number Z (for the particles of the material), specific surface S_o of the material (free surface to volume ratio of the porous material), size d of the interparticle contacts and the average pore radius r) are determined according to the porosity of the material Π , the normal local deformation h/D of the particles in the contact zone and the relations presented in $\lceil 6 \rceil$:

$$1 - \Pi = (1 - 2/Z)^2 / [8(1.077 - 1/Z - Z^{-1.16})(0.5 - h/D)^3]; (1)$$

$$S_0 = 6(1 - \Pi)\{1 - Z[h_0/D - d/D(h_0/D - h/D)]\}/D;$$
 (2)

$$r \approx 2\Pi/S_0$$
, (3)

where $h = h_o - 4h_o^2(1.5D - h_o)/(3d^2)$, $h_o/D = [1 - (1 - d^2/D^2)^{0.5}]/2$; h_o is the height of a spherical segment per contact, m; and, h is the local decrease of the diameter D of a particle due to the contact with another particle, m.

The experimental data in [9, 10] show that the initial structure of the powder material corresponds to random packing with the parameters $Z_r = 7.3$ and $\Pi_r = 0.37$ for smooth spherical particles (for rough, oblong or irregularly shaped particles, especially in highly disperse materials, the porosity can reach $\Pi = 0.4$ or more). We shall assume that the unit cells of a material are octahedral (the central particle touches four other particles on the top and bottom) with $\Pi = 0.348$ (the average value for two types of octahedral packing) but one contact is broken for 70% of the particles. Then the coordination number decreases to Z = 7.3, and the porosity increases to $\Pi = 0.373$. The pores form an approximately cubic structure.

We shall determine more accurately the structural parameters of the initial material, taking account of the nonuni-

formity of the molded material (this is a manifestation of the process of clusterization) with a normal distribution of the material particles over the coordination number, as follows.

Let the initial clusters be spherical on average. In accordance with [6] and the experimental data only three-layer clusters need be considered.

In a disperse system, as a result of nonuniform packing of the particles, clusters already form as the system is being formed (see Fig. 1). During sintering a completely internal layer of a cluster consisting of 12 nearest-neighbor particles and part of a second, outer layer are formed around particles with the maximum coordination number by means of capillary forces. We shall determine the volume fraction of the outer layer of the particles in a cluster, which determine the cluster and intercluster porosity, as a sum of the corresponding spherical sectors of a three-dimensional system. Let the distance l from the center of a cluster to the center of the particles of the outer layer be the arithmetic mean of the distance between two rows (layers) in simple cubic packing 2D and between two rows in hexagonal $[2(2/3)^{0.5}]$ packing, i.e., l = 1.82D.

Then, from the right triangle OO_nA in Fig. 1 we obtain OA = 1.89D. Next, since the triangles OO_nA and OCB are similar, we can find the height of the sector (equal to $D/2 - O_nC$) of a particle in the outer layer, determining the fraction of its volume in the inner part of the cluster. It equals approximately 0.43 times the volume of the particle. Using the number of neighbors in the first (Z+2) coordination group, we determine the statistical average number N of particles in the outer layer of the cluster:

$$N = 16 + 3Z/4 + Z^2/8$$
.

We now use the facts that Z=12 for the central particle of a cluster, Z=(12+Z)/2 for 12 particles in the middle layer and the total number of contacts $Z_{\Sigma}=12(12+Z)/2$. Then, for the outer layer Z in the cluster part can be taken to be the same as in the middle layer Z=(12+Z)/2. Hence the sum of the contacts of the outer layer with the particles of the cluster equals $Z_{\Sigma}=0.43\times0.5(Z+12)(16+3Z/4+Z^2/8)$, and the average coordination number $Z_{\rm cl}$ for the particles of the cluster can be expressed in the following form:

$$Z_{cl} = [12 + 6(12 + Z) + 0.215(12 + Z)(16 + 3Z/4 + Z^2/8)]/[13 + 0.43(16 + 3Z/4 + Z^2/8)].$$
 (4)

We shall use the proposed model to analyze the initial structure of a green part with point contacts between disperse particles with porosity Π .

Using the average porosity and the expressions (1) - (3) we shall calculate the average parameters of the structure Z, S_0 and r. Next, we shall use the normal distribution of the particles over the coordination number [6]

$$V(Z_s = Z) = 48; \quad V(Z_s = Z \pm 1) = 23; \quad V(Z_s = Z \pm 2) = 3 \quad (5)$$

for $Z \le 10$.

	Average	parameters		Parameters of the cluster structure					
Z	П	$S_{\rm o}$, μ m ⁻¹	r, µm	$Z_{\rm mic}/Z_{\rm mac}$	$\Pi_{\rm mic}/\Pi_{\rm mac}$	$S_{\rm o \ mic}/S_{\rm o \ mac}$	$r_{\rm mic}/r_{\rm mac}$		
6	0.476	0.314	3.033	6.280	0.4598	0.324	2.837		
				5.597	0.5063	0.296	3.418		
8	0.373	0.376	1.986	8.142	0.368	0.380	1.937		
				7.586	0.391	0.365	2.140		

TABLE 1. Average and Cluster Structure of Unsintered Ceramic Materials

Given the particle distribution in a cluster, the expression (5) can be used to calculate the average coordination number $Z_{\rm mic}$ of the particles (microstructure) for the inner part of a cluster and the average coordination number of the particles $Z_{\rm mac}$ (macrostructure) for the intercluster porosity.

As an example the parameters Z ($Z_{\rm mic}$ and $Z_{\rm mac}$), ($\Pi_{\rm mic}$ and $\Pi_{\rm mac}$), $S_{\rm o}$ ($S_{\rm o\,mic}$ and $S_{\rm o\,mac}$) and r ($r_{\rm mic}$ and $r_{\rm mac}$) calculated using the values of Π for a system of particles of size $D=10~\mu{\rm m}$ (for d=0) are presented in Table 1.

It follows from Table 1 that the radii of the capillaries in and between clusters differ appreciably.

During the sintering process the capillary forces in the clusters are stronger than in the intercluster space. The shrinkage of the cluster formations with the appearance of macroparticles in the material is only partial because the pores (capillaries) in the intercluster space become larger under the action of tensile stresses. As a result, together with shrinkage of the material, sharp increase of the coordination number in the clusters (porous particles) $Z_{\rm mic}$ and decrease of the microporosity $\Pi_{\rm mic}$ at the start of sintering the average size of the intercluster macropores increases.

We shall now obtain a method for calculating the parameters of the porous structure of a material as a function of its porosity during sintering, based on the following assumptions.

1. At the same time as the average coordination number of the particles in a material increases the sizes of the interparticle contacts d/D and, correspondingly, the local deformation h/D gradually increase. We assume that h/D increases linearly with decreasing porosity from the sizes of the contacts after the formation of a green part h_m/D to the maximum value $h_{\rm max}/D$, which for Z=12 with $\Pi=0$ is obtained using the relation (1) equal to 0.0474. We note that in the relation (1) the interparticle contacts are assumed to be cylindrical, and as porosity goes to zero the contact surface goes to a pentagonal surface. For this reason we shall refine Eq. (1) on the basis of the following considerations.

Two variants are possible as the porosity drops below $\Pi = 0.26$.

In the first variant a continuous structure comprised of elementary dodecahedra, whose unfinished edges form a capillary network comprised of connected tetrahedral pores. As sintering proceeds the coupled pores transform into isolated pores and can even vanish completely. The result is a continuous system of almost regular dodecahedra. The vo-

lume of a spherical particle $\pi D^3/6$ equals the volume of a regular dodecahedron with edge a. The volume and surface area of the latter are equal to $7.6631a^3$ and $20.6457a^2$, respectively. The volume of the dodecahedron can be expressed as $\pi D^3/6 = 20.6457a^2(0.5D - h_{\rm max})/3$. Hence we determine the maximum normal deformation in the contact zone as $h_{\rm max}/D = 0.0456$ at $\Pi = 0$.

The value obtained for h_{max}/D and the value according to the expression (1) for Z=12 and $\Pi=0$ are in the ratio 0.8718. Then the expression (1) assumes the form

$$1 - \Pi = (1 - 2/Z)^2 / [8(1.077 - 1/Z - Z^{-1.16}) \times (0.5 - 0.8718h/D)^3].$$
 (6)

In the second variant, as porosity drops below the value $\Pi = 0.26$ a continuous structure comprised of semiregular truncated octahedral is formed. The transformation of the lattice as $Z \rightarrow 14$ into a pore-free structure with $\Pi = 0$ can be represented as compaction of a powder structure owing to the interaction of the deformation of the particles with the formation of eight primary cylindrical contacts followed by six additional secondary contacts. The rectangular through channels gradually transform into interconnected tetrahedral pores. Subsequent compaction proceeds with the primary contacts transforming into hexagonal ones and secondary contacts into square ones. The result is a continuous structure comprised of particles in the form of semiregular truncated octahedra, whose edges form a tetrahedral capillary network with $Z_e = 4$. In addition, the capillaries (pores) around square contacts are wider than all other capillaries.

According to the expression (1) the maximum value $h_{\rm max}/D$ is 0.04243 for Z=14 with $\Pi=0$. For $\Pi=0$ a dense material comprised of semiregular truncated octahedra with edge m is formed. They are obtained by cutting off each regular octahedron with edge a=3m, whose volume and surface area equal $7.6631a^3$ and $20.6457a^2$, respectively, six tetrahedral pyramids with edges m.

The volume of a spherical particle $\pi D^3/6$ equals the volume of a semiregular truncated octahedron, which gives m = 0.359D. The heights of the six tetrahedral pyramids cut off equal $m \times 2^{0.5}$ and the areas of their bases equal m^2 . Hence we obtain that the distance from the center of a polyhedron to the hexagonal faces and tetragonal faces equals 0.4397D and 0.50775D, respectively. Since the areas of the square and hexagonal contacts are in the ratio 1:2.5981, we

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determine the average normal local deformation of the particles in the contact zone for $\Pi = 0$ as

$$H/D = [8(0.5 - 0.4397) \times 2.5981 + 6(0.5 - 0.50775)]/(8 \times 2.5981 + 6) = 0.0451.$$

The value of h/D according to the expression (4) for Z = 14 and $\Pi = 0$ equals 0.04245 or 0.9412 times the value obtained. Then the refined expression (1) becomes

$$1 - \Pi = (1 - 2/Z)^2 / [8(1.077 - 1/Z - Z^{-1.16}) \times (0.5 - 0.941 h/D)^3].$$
 (7)

Since the correction for $Z_{\rm max}=12$ (when the particles on average are regular dodecahedra) is larger than the correction in the expression (7), for low-porosity materials the model based on semiregular truncated octahedra is preferable, and for this reason we choose it.

The size of the contacts is set by the porosity of the system and the initial value of the average deformation of the particles in the contact zone h_m/D (or the average initial size of the contacts d_m/D) after formation:

$$h/D = h_m/D + 0.0451 - (0.0451 - h_m/D) \Pi/\Pi_m$$
. (8)

The average structural parameters Z, S_0 and r are calculated for the average porosity Π using the expressions (7), (8), (2) and (3) for particles of size D.

2. We assume that before the porosity of ceramic materials starts to decrease during sintering by capillary forces the first to form are dense internal regions with spherical (on average) particles (microstructure) with average coordination number $Z_{\rm mic}$ in the material equal to

$$Z_{\text{mic}} = (Z+3) \text{ for } Z \le 11 \text{ and } Z_{\text{mic}} = 14 \text{ for } Z \ge 11. (9)$$

We calculate the microporosity using the expressions (7) and (8). The micropore size $r_{\rm mic}$ is determined from the expression (3) with the values $\Pi_{\rm mic}$ and $Z_{\rm mic}$ for the microporous space.

3. To go beyond the cluster sizes given by the expression (4) we shall use from it only the initial ratio of the number $N_{\rm cl}$ of microparticles forming the microstructure of a cluster and the total number N_{Σ} of microparticles per unit volume containing one average cluster for the initial porosity of the material $\Pi = 0.373$:

$$N_{\rm cl}=13+0.43(16+3Z/4+Z^2/8)$$
 and $N_{\Sigma}=13+(16+Z/4+Z^2/8),\ N_{\rm cl}/N_{\Sigma}=25.1/43.1=0.582.$

The simplest expression for the volume of the material corresponding to the internal volume $V_{s\,\text{mic}}$ of a cluster that reflects the fractal character of clusterization is

$$V_{\text{s mic}} = (1 - 0.7\Pi)^{1.8}.$$
 (10)

4. Let us now examine a unit volume of the material containing a single macroparticle (one cluster).

The volume and average size of a macroparticle are given by

$$V_{s \text{ mac}} = N_{\Sigma} \pi D^{3} (1 + V_{p \text{ mic}}) / 6;$$

$$D_{\text{mac}} = D[N_{\Sigma} (1 + V_{p \text{ mic}})]^{1/3},$$
(11)

where $V_{p \; {
m mic}}$ is the pore volume in a macroparticle, determined from the expression for the microporosity

$$\Pi_{\rm mic} = V_{p \, \rm mic} / (V_{s \, \rm mic} + V_{p \, \rm mic}).$$

Hence the micropore volume Π_{mic} in a macroparticle and the macroporosity Π_{mac} of the material can be calculated from the expressions

$$V_{p \, \text{mic}} = V_{s \, \text{mic}} \, \Pi_{\text{mic}} / (1 - \Pi_{\text{mic}}); \, \Pi_{\text{mac}} = \Pi - V_{p \, \text{mic}}. \, (12)$$

5. We assume that $h_{\rm mac}/D_{\rm mac}$ in the macrostructure assumes the maximum value (equal to 0.0451), since the macrocontacts are formed by many microparticles in the outer layer of a macroparticle. Then the average coordination number $Z_{\rm mac}$ can be calculated from the expressions (7).

Next, the values of $S_{\rm o}$ and r are determined using the values of $\Pi_{\rm mac}$, $D_{\rm mac}$, $h_{\rm mac}/D_{\rm mac}$, $h_{\rm \hat{l}\,mac}/D_{\rm mac}$, $d_{\rm mac}/D_{\rm mac}$ and the expressions (2) and (3).

ALGORITHM FOR CALCULATING THE STRUCTURAL PARAMETERS

- 1. The average structural parameters are calculated for the average porosity Π :
- a) the size of the interparticle contacts h/D according to the expression (8);
- b) the values of d/D and $h_{\rm o}/D$ by iteration according to the expressions

$$h = h_o - 4h_o^2 (1.5D - h_o)/(3d^2)$$

and $d/D = 2[h_o/D(1 - h_o/D)]^{0.5}$;

- c) Z, S_0 and r according to the values of Π , h/D, h_0/D and d/D using the expressions (8), (2) and (3).
- 2. The parameters of the microporous structure are calculated:
- a) the average coordination number Z_{mic} by means of the expression (9);
- b) the microporosity Π_{mic} by means of the expressions (7) and (8);
- c) $S_{\rm o}$ and $r_{\rm cl}$ by means of the expression (2) and (3) for the values of $\Pi_{\rm mic}$, $Z_{\rm mic}$, h/D, $h_{\rm o}/D$ and d/D and the volume fraction $V_{s\,\rm mic}$ of particles in the microporous structure per unit volume of the system by means of the expression (10).
- 3. The parameters of the macroporous structure are calculated:
- a) the volume $V_{s \text{ mac}}$ and average size D_{mac} of a macroparticle by means of the expressions (11);

	Average structure						Micro- and macroporous structures					
				r, μm					g /g			
П	Z	h/D	$S_{\rm o}$, μ m ⁻¹	According to Eq. (6)	According to Eq. (3)	$\Pi_{ m mic}/\Pi_{ m mac}$	$Z_{\rm mic}/Z_{\rm mac}$	$D_{ m mac}$, $\mu{ m m}$	$S_{\text{o mic}}/S_{\text{o mac}},$ μm^{-1}	$r_{\rm cl}/r_{i{ m cl}}$		
0.37	7.30	0	0.376	1.981	1.988	0.289	10.3	36.59	0.427	1.354		
						0.137	7.93		0.141	1.938		
0.30	8.43	0.0088	0.366	1.641	1.760	0.231	11.43	36.23	0.380	1.212		
						0.104	8.75		0.128	1.619		
0.26	9.12	0.0136	0.352	1.482	1.659	0.197	12.12	36.07	0.347	1.137		
						0.089	9.19		0.120	1.484		
0.20	10.20	0.0209	0.315	1.272	1.457	0.146	13.2	35.85	0.284	1.030		
						0.070	9.8		0.104	1.336		
0.15	11.19	0.0268	0.269	1.114	1.261	0.105	_14	35.68	0.220	0.953		
						0.054	10.36		0.090	1.206		
0.10	12.13	0.0330	0.211	0.949	1.030	0.071	14	35.44	0.165	0.862		
						0.033	11.23		0.071	0.919		
0.05	13.09	0.0390	0.138	0.722	0.730	0.036	14	35.23	0.110	0.663		
						0.015	12.10		0.050	0.575		
0	14.00	0.0451	_	0	0	$\underline{0}$	14	_	_	_		
						0	1/1					

TABLE 2. Parameters of the Average, Microporous and Macroporous Structure of Unsintered Ceramic Materials

- b) the macroporosity Π_{mac} by means of the expression (12);
- c) the coordination number $Z_{\rm mac}$ (by iteration), the specific surface $S_{\rm o\ mac}$ and the average pore radius $r_{\rm mac}$ by means of the expressions (7), (8), (2) and (3) for the values of $\Pi_{\rm mac}$, $D_{\rm mac}$, $h_{\rm mac}/D_{\rm mac}$, $h_{\rm o\ mac}/D_{\rm mac}$ and $d_{\rm mac}/D_{\rm mac}$.

The parameters Z ($Z_{\rm mic}$ and $Z_{\rm mac}$), $\Pi_{\rm mic}$, $\Pi_{\rm mac}$, $D_{\rm mac}$, $S_{\rm o}$ ($S_{\rm o\,mic}$ and $S_{\rm o\,mac}$) and r ($r_{\rm mic}$ and $r_{\rm mac}$) for a model system of particles of size $D=10~\mu{\rm m}$ ($d_{m}=0$ for initial porosity $\Pi_{r}=0.37$) are presented in Table 2.

It follows from Table 2 that at the start of sintering the sizes of the macropores in and between clusters were more than 1/3-rd greater than the pore sizes with uniform sintering, after which as the porosity decreases below 15% the difference gradually decreases. For porosity below 0.25 the specific surface in a cluster becomes less that the intercluster specific surface.

CONCLUSIONS

- 1. The total and local compaction during sintering of ceramic materials was analyzed and a model for the sintering process in such materials and an algorithm for calculating the structural parameters for the compaction of these materials in the sintering process were developed.
- 2. The macropores are more than 1/4-th larger than the pore sizes for uniform sintering. For this reason, the decrease of the pore size in a material lags behind the shrinkage of the material during heat-treatment, which corresponds to the experimental data.

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